

* NOTICES *

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CLAIMS

[Claim(s)]

[Claim 1] The number b of mols of number [of this polyester polyol] a of mols, 1, and 4-butanediol and the number c of mols of diisocyanate are the following formula (I) about polyester polyol, 1, and 4-butanediol and diisocyanate of molecular weight 2500-3500.

$$1.01 \leq c/(a+b) \leq 1.10 \text{ (I)}$$

Mole fraction [of 1 / in / all diol component criteria / it has the diol component and dicarboxylic-acid component which are made to react at a rate which carries out ** satisfactory, and are obtained and which it is with an JIS-A degrees of hardness of 75 or more polyester system polyurethane, and this polyester polyol becomes mainly from 1 and 9-nonane diol component and a 3-methyl-1,5-pentanediol component, and], and 9-nonane diol component / d, and mole fraction e of a 3-methyl-1,5-pentanediol component are the

$$0.4 \leq d/(d+e) \leq 0.6 \text{ (II)}$$

Polyurethane characterized by carrying out ** satisfactory.

[Claim 2] Polyurethane according to claim 1 this diisocyanate of whose is 4 and 4'-diphenylmethane diisocyanate.

[Claim 3] Polyurethane according to claim 1 or 2 this polyester polyol of whose is a polyester polyol which this titanium system esterification catalyst was made to deactivate, and was obtained after carrying out the polycondensation of a diol and the dicarboxylic acid to the bottom of existence of a titanium system esterification catalyst.

[Claim 4] The manufacture method of the polyurethane moldings characterized by heat-treating at the temperature of 60 degrees C or more after fabricating polyurethane according to claim 1, 2, or 3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the moldings which consists of the polyurethane and this polyurethane which are excellent in thermal resistance, a compression set, and all cold-resistant performances. The polyurethane of this invention gives after fabrication the moldings which is excellent in thermal resistance, a compression set, and all cold-resistant performances only leaving it at a room temperature, and a performance gives after fabrication the moldings which improved further by heat-treating.

[0002]

[Description of the Prior Art] Since thermoplastic polyurethane has many features, such as excelling in high elasticity, abrasion resistance, and oil resistance, it attracts attention as alternate material of rubber or plastics, and is used so much for a use wide range as a molding material which can apply the usual plastic-molding processing method.

[0003]

[Problem(s) to be Solved by the Invention] However, among thermoplastic polyurethane, from a heat-resistant good thing being inferior in a compression set or cold resistance, when aiming at expansion of use expansion, thermoplastic polyurethane which reconciled thermal resistance, a compression set, and cold resistance is desired. Carrying out a deer, one of the purposes of this invention is to offer the polyurethane which is excellent in thermal resistance, a compression set, and all cold-resistant performances. Moreover, other purposes of this invention are to offer the manufacture method of a polyurethane moldings of demonstrating many of these outstanding performances effectively.

[0004]

[Means for Solving the Problem] According to this invention, for one of the above-mentioned purposes, the number b of mols of number [of this polyester polyol] a of mols, 1, and 4-butanediol and the number c of mols of diisocyanate are the following formula (I) about polyester polyol, 1, and 4-butanediol and diisocyanate of molecular weight 2500-3500.

[0005]

$$1.01 \leq c/(a+b) \leq 1.10 \text{ (I)}$$

[0006] Mole fraction [of 1 / in / all diol component criteria / it has the diol component and dicarboxylic-acid component which are made to react at a rate which carries out ** satisfactory, and are obtained and which it is with an JIS-A degrees of hardness of 75 or more polyester system polyurethane, and this polyester polyol becomes mainly from 1 and 9-nonane diol component and a 3-methyl-1,5-pentanediol component, and], and 9-nonane diol component / d, and mole fraction e of a 3-methyl-1,5-pentanediol component are the

[0007]

$$0.4 \leq d/(d+e) \leq 0.6 \text{ (II)}$$

[0008] It is attained by offering the polyurethane characterized by carrying out ** satisfactory. Moreover, other purposes of this invention are attained after fabricating this polyurethane by offering the manufacture method of the polyurethane moldings characterized by heat-treating at the temperature of 60 degrees C or more.

[0009] The polyester polyol used in this invention mainly consists of a diol component and a dicarboxylic-acid component, and this diol component mainly consists of a 1 and 9-nonane diol component and a 3-methyl-1,5-pentanediol component. It is important for 1 in this diol component, mole fraction [of 9-nonane diol component] d, and mole fraction e of a 3-methyl-1,5-pentanediol component to satisfy the above-mentioned formula (II). In the cold resistance of polyurethane falling when the value of $d/(d+e)$ is less than 0.4, and exceeding 0.6, thermal resistance and the performance of a compression set fall. Moreover, the molecular weight (number average molecular weight) of the polyester polyol used in this invention is within the limits of 2500-3500. The thermal resistance of the polyurethane obtained as the molecular weight of a polyester polyol is less than 2500, and the

performance of a compression set fall, and on the other hand, in exceeding 3500, the moldability, tensile strength, and transparency of the polyurethane obtained become inadequate.

[0010] As a dicarboxylic-acid component in the polyester polyol used by this invention, the straight chain aliphatic dicarboxylic acid of 6-12 has a desirable carbon number. As an example of this aliphatic dicarboxylic acid, an adipic acid, a pimelic acid, a suberic acid, an azelaic acid, a sebacic acid, etc. are mentioned. Moreover, although they may be only 1 and 9-nonane diol and 3-methyl-1,5-pentanediol, as long as the diol component is little, other diols may be additionally used for it.

[0011] Especially the manufacturing method of a polyester polyol cannot be limited, for example, can use a diol, dicarboxylic acids, or those esterification objects as a raw material, and can manufacture them by the well-known polycondensation method by the esterification reaction or the ester exchange reaction. In addition, it is possible to use esterification catalysts, such as a titanium catalyst and a tin catalyst, in this polycondensation. When a titanium system esterification catalyst is used, it is desirable to perform deactivation processing of this catalyst included in the obtained polyester polyol after a polycondensation. As deactivation processing, the method of contacting a polyester polyol in water under a heating condition is desirable.

[0012] In this invention, 4 and 4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, toluylene diisocyanate, 1, and 5-naphthylene diisocyanate etc. can be mentioned as usable diisocyanate, for example. Also in these, especially 4 and 4'-diphenylmethane diisocyanate is desirable.

[0013] Although a macromolecule polyol, a chain extension agent, and diisocyanate are made to react and it is obtained, in order to secure the outstanding thermal resistance and the outstanding compression set, and a cold-resistant performance in this invention, it is important for thermoplastic polyurethane to use 1 and 4-butanediol as the above-mentioned polyester polyol and a chain extension agent as a macromolecule polyol, respectively, and to set up a polyester polyol, a chain extension agent, and the amount of the relativity used of diisocyanate within limits which satisfy the above-mentioned formula (That is, since the molecular weight of polyurethane does not fully increase [the number b of mols of number / of this polyester polyol / a of mols, 1, and 4-butanediol, and the number c of mols of diisocyanate] after fabrication in the value of $c/(a+b)$ in being smaller than 1.01, only a moldings with inadequate thermal resistance and performance of a compression set is obtained. On the contrary, when the value of $c/(a+b)$ is larger than 1.10, the moldability of polyurethane becomes poor and the thermoplastic feature becomes is hard to be demonstrated. As for the value of $c/(a+b)$, it is desirable that it is within the limits of 1.02-1.08.

[0014] About the method of carrying out the polymerization of polyester polyol, 1, and 4-butanediol and the diisocyanate, and manufacturing the polyurethane of this invention, the technology of a well-known urethane-ized reaction is employable. Especially it is desirable to carry out a melting polymerization under un-existing [of a solvent] substantially, and the continuation melting polymerization using a multiaxial screw die pressing appearance machine is especially desirable. In addition, it faces manufacturing the polyurethane of this invention, and as a macromolecule polyol, a chain extension agent, and diisocyanate, as long as it is little, you may use together compounds other than above-mentioned polyester polyol and 1, and 4-butanediol. Moreover, you may add suitably additives, such as a coloring agent, lubricant, a crystalline-nucleus agent, a flame retarder, an ultraviolet ray absorbent, an antioxidant, a light-fast improvement agent, a hydrolysis-inhibitor, and an antifungal agent, after polymerization process or a polymerization.

[0015] In the polyurethane of this invention, in order to secure the outstanding thermal resistance and the outstanding compression set, and a cold-resistant performance, it is important that a degree of hardness (JIS-A) is 75 or more.

[0016] the polyurethane of this invention -- a logarithm -- it is desirable that viscosity (eta_{inh}) is in the range of 0.5 - 2.1 dl/g By considering as this range, the outstanding performance in thermal resistance, a compression set, and a moldability becomes much more remarkable. in addition, a logarithm -- viscosity can dissolve a sample in the N,N-dimethylformamide solution of the n butylamine of 0.05M so that it may become 0.5 g/dl, it can measure solution viscosity with a UBBERODE type viscometer at 30 degrees C 24 hours after, and can ask for it from the following formula

[0017] $\eta_{rel} = t/t_{0\eta_{inh}} = \ln(\eta_{rel})/ct$: Flowing-down time of a solution (second)
to : flowing-down time of a solvent (second)

η_{rel} : Specific viscosity c : Concentration of polyurethane (sample) (g/dl)

[0018] The polyurethane of this invention is excellent in thermal resistance, a compression set, and all cold-resistant performances. Being able to present fabrication of injection molding etc. with the polyurethane of this invention, the moldings obtained demonstrates many performances which were excellent in the above originating in the polyurethane of this invention. Furthermore, performances, such as a compression set, turn into temperature which is 60 degrees C or more and a moldings does not deform for the obtained moldings after fabrication, and a performance which was further excellent by heat-treating especially at the temperature within

the limits of 80–110 degrees C. Therefore, they are the mold goods which can be obtained from the former, such as a sheet, a film, a squeegee, a chain, a belt, a screen, a tube, the cleaning blade for a copy, an ejection roll, various rolls, a gear, an axle-pin rake, a binder, a solid tire, packing material, autoparts, a sole, sports shoes, adhesives, a machine part, a vibroisolating material, a sound deadener, and an elastic fiber, by injection molding used for fabrication of polyurethane, extrusion molding, etc. as a concrete use

[0019]

[Example] Hereafter, an example explains this invention concretely. In addition, in the example, a degree of hardness, thermal resistance, a compression set, and cold resistance were measured by the following methods.

[0020] It measured with the Shore A hardness meter using the forming sample with a thickness of 6mm obtained by [degree-of-hardness] injection molding.

[0021] The BIKATTO softening temperature was measured using the forming sample with a thickness of 4mm obtained by [heat-resistant] injection molding, and it considered as the heat-resistant index. The measuring load of a BIKATTO softening temperature set to 1kgf, and was measured according to JIS-K -7206.

[0022] It measured using the forming sample with a thickness of 20mm obtained by [compression set] injection molding by the method (heat treatment conditions : 70 degree-Cx 22 hours) based on JIS-K -6301.

[0023] The piece of a forming disk blank test with a thickness of 2mm obtained by [cold-resistant] injection molding was produced. The dynamic viscoelasticity of this test piece was measured on the frequency of 11Hz, and the dynamic loss modulus (E'') considered as the cold-resistant index in quest of the temperature (T_{α}) used as a peak.

[0024] The dumbbell specimen created from the forming disk with a thickness of 2mm obtained by [adding-water-proof resolvability] injection molding was left for three weeks under 70 degrees C and 95% of relative humidity, the breaking strength of the test piece in it order was measured, and it considered as the index of adding-water-proof resolvability in quest of the retention of the intensity after the neglect to the intensity before this neglect.

[0025] The compound used in the example was shown using the cable address. The compound name which a cable address means is shown in the following table 1.

[0026]

[Table 1]

略号	化合物
BD	: 1, 4-ブタンジオール
MPD	: 3-メチル-1, 5-ペンタンジオール
ND	: 1, 9-ノナンジオール
PNMA	: ND, MPDおよびアジピン酸から得られたポリエステルジオール
MDI	: 4, 4'-ジフェニルメタンジイソシアネート

[0027] [The example 1 of reference] (manufacture of PNMA-A)

ND1920g, MPD1416g, and 2920g of adipic acids were taught to the reactor, and the esterification reaction was performed under reduced pressure, distilling off the water generated at 200 degrees C out of a system. The polycondensation reaction was started having added tetrapod isopropyl titanate 90mg and decompressing to 200 - 100mmHg, when the acid number of a reactant became 30 or less. When the acid number was set to 1.0, the degree of vacuum was gradually raised with the vacuum pump, and the reaction was completed. Consequently, number average molecular weight 3000 and 5090g of PNMA(s) of ND/MPD=1 / 1 (mole ratio) were obtained (the polyester diol obtained here is hereafter called "PNMA-A").

[0028] [The example 2 of reference] (deactivation of a titanium system catalyst)

PNMA-A5000g obtained in the example 1 of reference was heated at 100 degrees C, and 150g (3 % of the weight) of water was added to this. Stirring, by continuing heating for further 2 hours, the titanium system catalyst was made to deactivate and water was distilled off under reduced pressure (the polyester diol obtained by this processing is called "PNMA-B").

[0029] Except changing the diol which carries out the [examples 3-7 of reference] use, according to the examples 1 and 2 of reference, esterification reaction, polycondensation reaction, and catalyst deactivation processing were performed, and the polyester diol was obtained, respectively. The diol component and molecular weight (number average molecular weight) of a polyester diol which were obtained are shown in Table 2, respectively.

[0030]

[Table 2]

	ポリエステルジオール	ジオール 成分 (モル比)	テタン系触媒 先活	分子量
参考例 3	PNMA-C	ND/MPD (60/40)	有り	3010
参考例 4	PNMA-D	ND/MPD (50/50)	有り	2065
参考例 5	PNA -A	ND	有り	3025
参考例 6	PMPA-A	MPD	有り	3005
参考例 7	PBA -A	BD	有り	3030

[0031] MDI which carried out heating fusion should be shown in the following table 3 at PNMA-B and BD which were obtained in the example 2 of [example 1] reference, and 50 degrees C. From the metering pump, it taught continuously the 2 shaft screw die pressing appearance machine which rotates in the direction of the same axle of ratio-of-length-to-diameter=36 by 30mmphi, and continuation melting polymerization reaction was performed at the temperature of 260 degrees C so that it might be 1:5.60:6.86 in the mole ratio of PNMA-B:BD:MDI and these total amounts might serve as 200 g/min. The melt of the generated thermoplastic polyurethane was underwater extruded continuously by the shape of a strand, and, subsequently it cut by the pelletizer, and fabricated on the pellet. after carrying out injection molding of this pellet at 200 degrees C after 20-hour moisture absorption and drying by 80 degrees C, producing the sample for measurement and leaving it for one week at 8 hours or 20 degrees C in 80 degrees C — a logarithm — viscosity, a degree of hardness, thermal resistance, a compression set, and cold resistance were measured The obtained result is shown in the following table 4.

[0032] Except adopting the conditions shown in Table 3 as the kind of [examples 2-4] polyester diol, and an operating rate of each raw material compound, a polymerization and pelletizing were performed like the example 1, and the pellet of thermoplastic polyurethane was obtained, respectively. The dryness and injection molding of a pellet which were obtained were performed like the example 1, and the physical properties of the sample left for one week at 8 hours or 20 degrees C in 80 degrees C were measured. The obtained result is shown in Table 4.

[0033] Except adopting the conditions shown in Table 3 as the kind of [examples 1-7 of comparison] polyester diol, and an operating rate of each raw material compound, a polymerization and pelletizing were performed like the example 1, and the pellet of thermoplastic polyurethane was obtained, respectively. The dryness and injection molding of a pellet which were obtained were performed like the example 1, and the physical properties of the sample left for one week at 8 hours or 20 degrees C in 80 degrees C were measured. The obtained result is shown in Table 4.

[0034]

[Table 3]

	ポリエステルジオール (A) (モル)	MDI (モル)	BD (モル)	MDI A+BD (モル比)
実施例 1	PNMA-B (1.0)	6.86	5.60	1.04
実施例 2	PNMA-B (1.0)	7.13	5.60	1.08
実施例 3	PNMA-C (1.0)	6.86	5.60	1.04
実施例 4	PNMA-B (1.0)	3.02	1.90	1.04
比較例 1	PNMA-B (1.0)	6.53	5.60	0.99
比較例 2	PNMA-D (1.0)	4.58	3.40	1.04
比較例 3	PNA -A (1.0)	6.86	5.60	1.04
比較例 4	PMPA-A (1.0)	6.86	5.60	1.04
比較例 5	PBA -A (1.0)	6.86	5.60	1.04
比較例 6	PBA -A (1.0)	3.02	1.90	1.04

[0035]

[Table 4]

	成形物物性					
	アニーリング条件 (20℃×1週間)		アニーリング条件 (左: 80℃×15時間/右: 20℃×1週間)			20℃×1週間
	硬度 (JIS-A)	耐寒性 (℃)	η_{inh} (dl/g)	耐熱性 (℃)	圧縮永久変 形 (%)	耐加水分解性 保持率 (%)
実施例 1	91	-46	1.45/1.35	162/160	20/31	92
実施例 2	92	-48	1.49/1.45	164/160	17/29	93
実施例 3	90	-44	1.42/1.35	166/161	18/26	92
実施例 4	75	-52	1.44/1.42	125/110	9/25	88
比較例 1	90	-45	0.85/0.82	132/129	39/55	72
比較例 2	92	-35	1.43/1.32	122/116	35/53	89
比較例 3	91	-15	1.34/1.28	172/168	21/32	95
比較例 4	90	-55	1.42/1.32	139/133	37/50	68
比較例 5	90	-42	1.43/1.33	119/110	45/70	45
比較例 6	75	-56	1.42/1.32	85/72	18/42	61

[0036] From the above-mentioned table 4, the polyurethane of this invention understands a bird clapper as the compression set of a moldings being much more good with heat treatment after excelling in thermal resistance, a compression set, and all cold-resistant performances, and fabrication (examples 1-4). On the other hand, with the polyurethane which is different from this invention in the molecular weight of the diol component of a polyester diol, and a polyester diol, or the amount of the relativity used of a polyurethane raw material compound, it turns out that at least one performance is poor thermal resistance, a compression set, and among cold resistance (examples 1-7 of comparison).

[0037]

[Effect of the Invention] According to this invention, the high degree-of-hardness polyurethane which is excellent in thermal resistance, a compression set, and all cold-resistant performances is offered. The moldings which consists of this polyurethane demonstrates the further excellent performance by heat-treating.

[Translation done.]

Polyurethane

Günter Oertel



Polyurethane Handbook

Chemistry – Raw Materials – Processing
Application – Properties

Edited by Günter Oertel

2nd Edition

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One-component PU industry sealants are mainly based on MDI prepolymers with a low NCO content. In the structural sealant market, these materials can be "pregelled" at 80–110°C (176–230°F) to a reactive, water-crosslinking hot melt, and are becoming well established. They contain sub-stoichiometric amounts of a heat-sensitive hardener (semi-thermic systems) [65, 66].

To formulate car body seam sealers, PU-based, thermic crosslinking one-component systems are used (curing at 130–160°C) (266–320°F). These systems are made from a combination of a blocked aromatic isocyanate prepolymer with a cycloaliphatic diamine [67] or from a fine dispersion of a solid diisocyanate. They are microencapsulated TDI uretdiones [68] in a liquid resin, for instance, a hydroxy or an aminofunctional polymer with a functionality of at least 2.

8.2 Thermoplastic Polyurethanes

H.-G. Hoppe, Dr. H.-G. Wussow

Polyurethane elastomers with thermoplastic character were first described in the 1950s. In the early 1960s they became commercially available. Today they are one of the most versatile products in the group of engineering thermoplastics with elastomeric properties. These materials allow the production of elastomeric articles by thermoplastic processing techniques. With increasing hardness the elastomeric character decreases but without changing the typical properties of PU (abrasion resistance, oil and heat resistance).

Thermoplastic deformation is repeatable plastication by the influence of temperature and pressure. One essential requirement is the reversible melting of the hard segments without thermal degradation. The macromolecules have to be linear; branched elastomers or thermosets cannot be repeatedly thermoformed. From bifunctional isocyanates, chain extenders and long-chain polyols, virtually unbranched molecules having a molecular weight of more than 15,000 are formed. By varying the amounts of hard and soft segment, the properties can be varied over a wide range without resorting to plasticizers.

8.2.1 Production

MDI is by far the most important diisocyanate used in the production of TPU. Only in special cases are TODI, HDI and IPDI are used, the last two for manufacturing light stable materials. Generally, 1,4-butane diol is used as the chain extender. Ethylene glycol, 1,6-hexane diol and 1,4-bis- β -hydroxyethoxybenzene (HQEE) are of limited significance in this area. Diamines are used only in special cases as chain extenders. The TPU products from these diamines have such a high melting point that they cannot be processed by normal thermoplastic methods without decomposition of the material.

Table 8.6. Long-Chain Polyols for the Production of TPU Products. Glass Transition Temperatures T_g and Melting Points T_m of 2,000 Molecular Weight Polyols

Polyols	T_m (°C)	(°F)	T_m (°C)	(°F)
Poly (propylene glycol)	– 73	– 99	–	–
Poly (tetramethylene glycol)	– 100	– 148	32	90
Poly (1,4-butane diol adipate)	– 71	– 96	56	133
Poly (ethandiol-1,4-butane diol adipate)	– 60	– 76	17 (37)	63 (99)
Poly (1,6-hexane diol-neopentyl glycol adipate)	– 57	– 71	27	81
Poly (ϵ -caprolactone)	– 72	– 98	59	138
Poly (1,6-hexane diol carbonate)	– 62	– 80	49	120

Many polyesters and a few polyethers can be used as the polyol component (see Tables 8.6 and 8.7).

8.2.1.1 Laboratory Preparation

The starting materials can be reacted in a simple pot. Materials such as mold release agents, antioxidants, UV absorbers, dyestuffs, catalysts and so on can be added. The polyols together with the additives are first charged, and the diisocyanate and chain extender are quickly added while stirring (one-shot method). In the prepolymer method, the polyol is first reacted with excess diisocyanate, and the chain extender is subsequently added to complete the reaction. The starting temperature is 60–120°C (140–250°F), and rises to 200°C (392°F) during the course of the reaction.

Table 8.7. Comparison of Properties of PU Elastomers Based on Polyester vs. Polyether (Shore Hardness from 75 A to 60 D)

Property	Polyester	Polyether
Wear resistance	+	—
Load bearing, compression set, etc.	+	—
Low temperature flexibility	—	+
Hydrolytic resistance	—	+
Heat aging	+	—
Swelling in oil, grease, solvents, water	+	—
O ₂ , O ₃ and U.V. stability	+	—
Stability to energetic radiation	+	—
Microbe and fungus resistance	—	+

+ favorable
— unfavorable

The reacted mass is postcured, cut, and granulated. Processing is described in the following chapter.

8.2.1.2 Technical Production

For the production of TPU in large quantities, a continuous process [69] is preferred to a discontinuous process. In the latter process, the raw materials are mixed and cast on a moving belt where they further react and become solid. The slabs are cooled, broken, and ground in a granulator. The irregular granules obtained can be converted to a uniform consistency (cylindrical or spheroidal) by extrusion and granulation. Reaction in a twin extruder is also an option [70 to 72]. In this method the TPU can be produced and converted to a regular pellet form in one step.

8.2.1.3 Mixtures with Other Materials

Polar polyurethane thermoplastics can be mixed with other thermoplastics and processed as a polymer blend. The components do not have unlimited miscibility (depending on the polarity of the thermoplastic). PVC, ABS, and polycarbonate as polar materials show good compatibility with TPU. Non-polar materials such as polyethylene and polypropylene show a tendency to separate from the mixture.

Brittle thermoplastics such as polyoxymethylene can be improved in terms of impact resistance and reduced in stiffness by adding small amounts of TPU.

Soft grades of TPU are used as non-migrating plasticizers in PVC. These PVC-TPU blends possess the same advantages as plasticizer-free polymers and do not cause stress cracking in contact with other plastics such as polycarbonate. Additional advantages are low temperature flexibility, abrasion resistance and oil resistance.

The same general rule as for thermoplastics applies to the compatibility of TPU with rubber. Non-polar products such as EPDM, butadiene and isoprene rubbers are not compatible with TPU. Nitrile and styrene-acrylonitrile rubbers exhibit good miscibility with TPU [73, 74].

8.2.2 Processing

Generally, thermoplastic polyurethanes are supplied as ready-to-use pellets. They are processed by methods and with apparatus traditionally used in the thermoplastics industry. The most important processing methods are injection molding, extrusion and calendering (sheet melting equipment). The different processing techniques all place specific requirements on the material. Special grades are necessary for some processes.

8.2.2.1 Preparation of the Pellets

Dry pellets can be used without preparation. Moist pellets must be dried before use. This can be done in a flash dryer or forced air drying oven at 100 to 110°C (212–230°F) for 30 min. to 2 hr. The maximum allowable moisture content for processing is approximately 0.1%. TPU pellets absorb about 0.5% water under normal climatic conditions when stored open to the air.

8.2.2.2 Post-Treatment of the Finished Parts

TPU parts attain their optimum properties after a thermal post cure. This applies especially to their recovery (compression set). According to the material type and configuration of the part, a post cure at 80–120°C (176–248°F) for 15–20 hr. is generally sufficient. Without post cure, the part should be stored 4 to 6 weeks at temperatures above 20°C (68°F) before it is put into service.

8.2.2.3 Use of Scrap and Regrind

Sprues, runners, and reject parts can be reground and mixed with virgin material for reuse in injection molding. Because of the possibility of slight thermal degradation, generally only 10 to 30% regrind is added. Processing of 100% regrind is possible. The reprocessed scrap should not be contaminated. In addition, predrying the regrind is often necessary. Mixtures of regrind and virgin material often give inhomogeneous extrusions. Therefore it is customary to use extrusion scrap for injection molding or to extrude 100% regrind as long as reduced mechanical properties are permissible for the articles produced.

8.2.2.4 Addition of Colorants

Thermoplastic polyurethanes are normally supplied as natural pellets. Colorants can be worked in during plastication in the barrel of the processing machine. Suitable colorants are inorganic and a few organic pigments, which are mixed with the TPU pellets as a color concentrate in pellet form or as a color paste. It is also possible to work with unbound pigments, but this is an infrequent practice due to their ease of separation and dust nuisance. Color concentrates in pellet form based on TPU are advantageous. Polystyrene color pellets are less suitable. Polyethylene and polyvinyl chloride color pellets are not compatible with TPU. They are generally used in the following amounts:

Color pellets: 1 to 4%

Color pastes: 0.5 to 1%

Pigments: 0.2 to 0.5%

At these levels a machine with a good plastication screw will give homogeneously colored extrusions and injection molded parts. A static mixer installed between the screw and nozzle.

7.3 Flexible Integral Skin and RIM Materials

Dr. G. Avar, Dr. A. Freitag, Dr. H. Lüdke, Dr. H.-J. Meiners, Dr. P. Seifert, Dr. Ch. Weber

7.3.1 Chemistry and Raw Materials

Flexible integral skin foams and RIM products are produced from two-component systems. One component consists of a mixture of isocyanate-reactive compounds and necessary additives, the other component is the isocyanate. The following describes the raw materials in detail:

Polyisocyanates

The isocyanates used for the manufacture of flexible PU integral skins are based mainly on diphenylmethane-4,4'-diisocyanate (MDI) or aliphatic diisocyanates, e.g. isophorone diisocyanate (IPDI). For the most part, diphenylmethane-4,4'-diisocyanate liquified by urethane or carbodiimide formation, and mixed with higher-functional components as appropriate, is used.

Because of different manufacturing processes, isomer distributions, and functionality of the polyisocyanates, there is a large number of different products (see chapter 3). Essential for processing are knowledge of the isocyanate content (%NCO) and viscosity.

Composition of the Isocyanate-Reactive Components

Polyether Polyols

The polyols used in the production of flexible integral skin foams have molecular weights between 2,000 and 8,000. Preferred starters are propylene glycol, trimethylolpropane and glycerine. Because short cure times are desired in the production of molded parts, active polyethers must be used.

In addition to polyhydroxyl polyethers accessible by alkoxylation of polyfunctional alcohols or amines, one also encounters polymer dispersions (styrene/acrylonitrile copolymers or polyureas) in polyethers [11]. Polyethers, among others, are characterized for processing by hydroxyl number (OH number), water content, and viscosity.

Polyester Polyols

Adipic acid polyesters are used in production of polyester PU parts, e.g. for the shoe industry. Ethylene glycol, diethylene glycol or butanediol – usually in mixtures – is used as glycol component. The polyesters are largely linear in structure and contain at most only a small quantity of trimethylolpropane or glycerine for crosslinking. Molecular weights lie between 2,000 and 4,000.

NH₂-Terminated Polyethers

The development of RIM technology to higher and higher machine outputs (see subsection 7.2) and the introduction of diamine-crosslinked RIM materials [12] made possible the processing of long chain polyethers with reactive amino-end groups [13, 14]. In practice, polyethers with aliphatic [15] or aromatic [16] amino groups are used for these RIM materials with high polyurea content. A further possibility for adjusting the reactivity of such "polyamine" systems is offered by converting the amino groups to ketimino groups. The RIM material thus contains polyurea/amide structures [17, 18].

Table 7.4. Influence of the Concentration of Milled Glass Fibers with and without Coating on the Properties of Flexible PU Integral Skin Foams (DETDA-Crosslinked Microcellular PU Elastomers)

Glass fiber			MF 7901	MF 7906		
Average fiber length (μm)			180	140		
% glass content in final product			22	17	22	26
Glass fiber			—	+	+	+
Properties	Dimensions	Temp.				
Density (DIN 53 420)	g/cc	RT	1.27	1.20	1.27	1.32
Shore D hardness (DIN 53 505)		RT	70	70	71	72
Flexural modulus (ASTM-D 790)	MPa	RT	1500	1400	1700	1900
Tensile strength (DIN 54 504)	MPa	RT	28	33	36	39
Elongation at break (DIN 53 504)	%	RT	130	35	20	15
Heat sag*	mm	160 °C	23	16	14	12
Coefficient of thermal expansion (VDE 0304/1)	$\times 10^{-6}/\text{K}$	-40 to +80 °C	48	50	40	35
Longitudinal shrinkage	%	RT	0.35	0.35	0.25	0.20
Impact strength (DIN 53 453)	kJ/m ²	-30 °C	20	12	12	11

* Cantilever beam arrangement; distance between supports: 150 mm

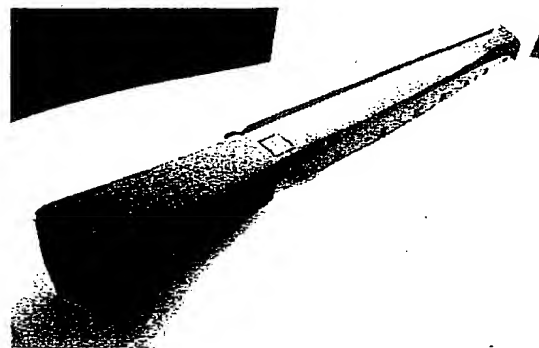


Fig. 7.22. Rocker panel for the Mercedes-Benz 200 series

7.3.3 Properties

7.3.3.1 Shoe Industry

PU integral skin foams have found wide use in the shoe industry. Two areas of application can be distinguished:

7.3.4 Production and Application of Molded Parts

7.3.4.1 Shoe Industry

Because of their range of physical properties, flexible integral skin foams can be used for almost all types of shoe soles and inserts. The raw material systems can be classified, on purely practical grounds, into the following groups:

1. Systems for street and leisure shoe soles:

These are made with either polyethers or polyesters.

Molded densities lie in the area of 0.5 g/cm^3 .

2. Systems for unit soles in sport shoes and other abusive applications:

These are almost exclusively based on polyester polyols, densities are about 0.6 g/cm^3 .

3. Systems for dual density sport shoe soles and other highly wear-resistance types:

Here also, one sees almost exclusively polyester polyol systems, where the density of the outer sole is near 1.0 g/cm^3 and that of the midsole between 0.35 and 0.45 g/cm^3 .

4. Systems for unit or dual density soles with special properties, e.g. enhanced low temperature flexibility, antistatic properties, increased thermal stability.

5. Systems for semirigid or rigid shoe inserts in densities around 0.25 g/cm^3 and systems for soft, elastic midsoles and wedges in the density range between 0.3 and 0.4 g/cm^3 .

6. Systems for miscellaneous applications, e.g. innershoes, cushioning parts and slip soles.

The following properties of flexible PU integral skin foams for use as soling material should be emphasized:

- Low density and thus low shoe weight
- Variable hardness
- Good elasticity and damping behavior
- High abrasion resistance

The low density contributes to the reduction of the total weight of a shoe. This improves the comfort of the shoes. Soft elastic integral skin foam has the advantage of distributing evenly the pressure of the foot during walking and standing and is therefore more comfortable as soling material. A picture of the distribution of foot pressure from the Institute of Work Physiology at the Technical University of Munich (Fig. 7.27) shows, by means of colored isobars, a lower concentration of pressure with soles made with integral skin foam compared with the pressure distribution with other hard soling materials. However, to avoid an undesired pronation or supination (i.e., a pushing of heel to toe, respectively inward or outward) during the foot's roll, the hardness of a shoe sole must be adjusted very exactly to both support and protect the foot.

The pleasant feel imparted to shoes by integral skin soles is also determined by the elasticity and the damping capabilities of the material. Permanent elastic deformability of the sole is important in cushioning the kinetic energy, and avoiding pressure points, when the foot is planted.

The high resistance to wear of integral skin soles is a complex property, which encompasses many more easily described individual properties. Chief among these is the abrasion resistance, but also the behavior on repeated bending, tear propagation resistance, tear resistance, and cut growth.

The fact that, by changing the density, the properties required by the given application can be achieved is used in the production of dual density soles. In this way, an unfoamed or nearly solid polyurethane outersole guarantees a high resistance to tear propagation, while a cellular, soft, elastic midsole offers comfort and low total weight.

Special requirements, as for example low temperature flexibility or thermal, hydrolytic and microbial stability, oil, fuel and solvent resistance, as well as antistatic properties, are met by the proper choice of raw materials or by addition of corresponding additives.



Fig. 7.27. Distribution of pressure over the sole of the foot (left: when standing on a hard surface; right: when standing on Bayflex flexible integral skin foam). Light areas = low pressure; dark areas = high pressure

Tests

The physical and chemical properties are measured by standardized test methods, which are described in (among others) DIN specification 53543 (see also chapter 9, test methods). For safety shoes, further special requirements are described in DIN specification 4843, such as electrical resistance, stability towards various media and specific construction requirements. Along with determining the properties of the pure material, the testing of the finished parts corresponding to their end uses under conditions similar to those in practical use are of great significance. The test methods developed for these purposes are, however, not standardized and are prescribed predominately for comparison testing and statements about correlations (see also chapter 9 on testing of finished parts).

Construction Guidelines

In the construction of integral skin soles, a design appropriate to the material must be observed. Sole thickness and profile design must be considered with regard to the chosen material. In the bending of thicker soles, higher stress and strain will occur, of course, than with thin soles. The sole thickness, measured in profile, should not exceed 8 mm. This is more critical in hard systems than in soft ones.

Sharp edges in the profile valleys and in the transition from sole to heel in the shank region must be avoided. The ratio of the profile rise to profile valley must be equal to or less than 1:1 (Fig. 7.28).

In profile design, one should be careful that the profile valleys do not run parallel to the bending line (Fig. 7.29).

In soles with a large pitch (that is the difference between the heel height and the thickness of the sole in the region of the ball of the foot), the bending stress is usually less because of the smaller effective bending angle than with flat soles (Fig. 7.30). In shoes with open heel parts, the stress on the sole is likewise less, because the sole does not follow the bending angle of the foot completely.

Manufacturing Processes

Fundamentally, the production of separate soles is distinguished from the direct attach process. In the former case, so-called molded soles, or unit soles, are produced, which are then glued, or otherwise fastened, to the upper. In the latter process, the upper functions as the

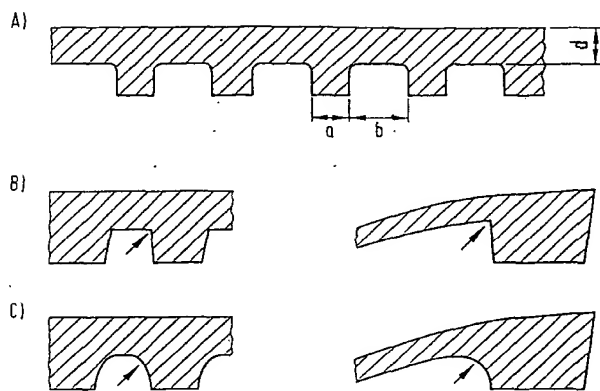


Fig. 7.28. Tread design

A) Thickness of sole at bottom of tread channels $d \leq 8$ mm, ratio of tread width to channel width $a:b \leq 1:1$

B) Poor designs

C) Good designs

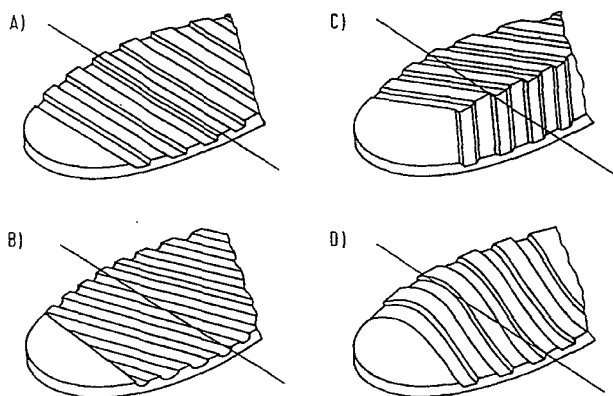


Fig. 7.29. Tread design

A) Tread running parallel to the flex line - poor design; B)-D) Treads running at an angle to the flex line - good design

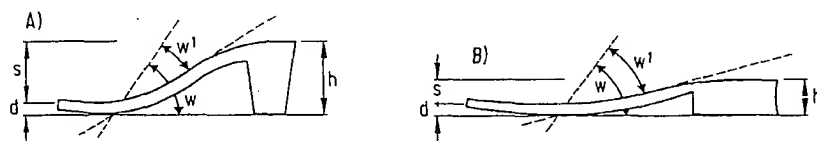


Fig. 7.30. Changes in the effective flexing angle due to differences in pitch
 h : height of heel; d : sole thickness; s : pitch; w : maximum possible flexing angle; w^1 : actual flexing angle determined by pitch

cover of the mold, so that the liquid polyurethane reaction mixture wets the upper, and the fully reacted sole is tightly bonded to the upper already at demold. These manufacturing processes are differentiated in their respective machinery and processing steps.

By far, the most common process in the production of molded soles is pouring into open molds. Thus the reaction mixture is poured via a vertically oriented, movable mixhead (see subsection 4.3.4) into the open molds, which are then closed for the duration of the curing process. The tools are mounted on a movable roundtable and brought one after the other into the pour position. With older so-called peripheral units, the tools are arranged in an arc, and the mixhead is moved from one mold station to the next (see also subsection 4.2.2). After demolding, the soles are normally degreased, coated by spraying or immersion, further worked in the case of special treatments (brushing, wiping, matting) or special surface effects, and the surface to be attached to the upper prepared (by roughening, priming, etc.). In the direct attachment process, one finds almost exclusively the rotating carousel with one or two machines with horizontally oriented mixheads for, respectively, unit or dual density

PATENT
1422-0477P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant:	Minoru SAWAI et al.	Conf.:	3707
Appl. No.:	09/859,419	Group:	1711
Filed:	May 18, 2001	Examiner:	J.M. COONEY
For:	POLYURETHANE FOAM		

LARGE ENTITY TRANSMITTAL FORM

Commissioner for Patents
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June 18, 2003

Sir:

Transmitted herewith is a Reply in the above-identified application.

- ☐ The enclosed document is being transmitted via the Certificate of Mailing provisions of 37 C.F.R. § 1.8.
- ☐ The enclosed document is being transmitted via facsimile.

The fee has been calculated as shown below:

	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR		PRESENT EXTRA	RATE	ADDITIONAL FEE
TOTAL	12	-	20	=	0	\$ 18	\$0.00
INDEPENDENT	1	-	3	=	0	\$ 84	\$0.00
<input type="checkbox"/> FIRST PRESENTATION OF A MULTIPLE DEPENDENT CLAIM						\$280	\$0.00
						TOTAL	\$0.00

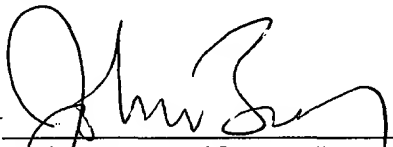
Appl. No. 09/859,419


- ☒ Petition for three (3) month(s) extension of time pursuant to 37 C.F.R. §§ 1.17 and 1.136(a). \$930.00 for the extension of time.
- ☐ No fee is required.
- ☒ Check(s) in the amount of \$930.00 is(are) enclosed.
- ☐ Please charge Deposit Account No. 02-2448 in the amount of \$0.00. This form is submitted in triplicate.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 
John W. Bailey, #32,881


JWB/KLR:gml
1422-0477P

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Attachment(s)

(Rev. 04/30/03)